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(54) Title: A PAD FOR CHEMICAL-MECHANICAL POLISHING AND APPARATUS AND METHODS OF MANUFACTURE THEREOF (57) Abstract <p>A polishing pad is provided for chemical-mechanical polishing widely used in the semiconductor industry. The pad material is hexagonal boron nitride and its composite. The pad is in the shape of a disc, a ring, or any plate having one or more openings. The pad can have a configuration of either two layers or three layers. The abrasive particles may be or may not be added in the pad materials. The high modulus of the pad leads to a high planarization within a die. The flexible design of the pad leads to a high polishing uniformity within a wafer surface.</p>		

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A PAD FOR CHEMICAL-MECHANICAL POLISHING AND APPARATUS AND METHODS OF MANUFACTURE THEREOF

TECHNICAL FIELD

The present innovation relates to devices used in the semiconductor industry for manufacture
5 of semiconductor chips and devices, and in particular to pads for chemical-mechanical
polishing of silicon wafers and dielectric and conductive materials formed on the wafer.
More specifically the invention relates to the application of high purity hexagonal boron
nitride (h-BN) and composites of h-BN and other ceramics with a porous structure in
chemical-mechanical polishing, as well as methods of processing and manufacture thereof.

BACKGROUND OF THE INVENTION

Chemical-mechanical polishing is widely used in the semiconductor industry. Generally,
integrated circuit (IC) chips are fabricated on silicon wafers. Transistors are made on the
polished wafer surface by a series of processing procedures, of which photolithography is the
primary step. The oxidation of silicon, the deposition of dielectric and conductive materials,
15 masking, etching, and the like are also included.

Polishing materials can not be metals due to the potential for causing a short circuit. A pad is
also not made of normal ceramics, which are so hard that they can cause scratching on the
surface of a wafer. Polymers include thermosetting and thermoplastic resins, elastomer (such
as rubber), and biopolymers (such as proteins). At present, thermosetting resins are
20 extensively used as pad material. Polyurethane foam with open pores is the most popular
pad material. One of the disadvantages of polymer materials, especially foam materials, is
their lack of rigidity. Deformation of the pad makes the die surface rough. Dishing occurs on
the surfaces of softer materials and lower portions of the patterns. This disadvantage makes
the next processing procedure difficult, or sometimes even impossible.

On the other hand, regular advanced ceramics have very high levels of strength, hardness as well as thermal and chemical resistance. Their main disadvantages or shortcomings, however, are high brittleness, low thermal shock resistance, and high manufacturing cost.

The high brittleness and low thermal shock resistance of advanced ceramics can be attributed to their crystal structure. The covalent bonding and ion bonding in ceramic crystals make internal dislocations difficult to form and move around, compared to dislocations in metals. This leads to the failure of ceramics by way of fracture rather than deformation. This intrinsic disadvantage limits their applications, especially as structural materials.

Among advanced ceramics, hexagonal boron nitride has a hexagonal layer structure similar to that of graphite. Within each hexagonal plane, the atoms are strongly bonded by covalent bonding. Between the planes, the atoms are weakly bonded by *Van Der Waals* force, which makes the material soft. Hexagonal boron nitride is the only soft engineering ceramic. The bending strength of its sintered body is 83 MPa. The elastic modulus is 20 GPa. These values are much lower than normal ceramics (several hundred MPa and over 100 GPa, respectively). Therefore, hexagonal boron nitride and composites including it can increase the rigidity of the polishing pad, but in the meantime, will not result in scratching on the die surface.

In certain fields such as the semiconductor and chemical industries, advanced ceramics are simply too hard to be useful. This is also true even with h-BN containing metal oxides: metal oxides used as sintering additives are also hard enough to cause scratching on the surface of wafers. Reduction of the need for metal and B_2O_3 to aid in densification in manufacturing ceramic electrode materials has been recommended in the art, as exemplified in Bannister et al. (1989, Ceramic International 15:375-382).

Another important technical requirement of the polishing process, other than local planarization within a die, is the polishing uniformity of the entire wafer surface. During polishing processing as shown in Fig. 4, the edge portion of the wafer is polished faster than the central portion, and the pads are also unevenly worn away under unevenly distributed back pressure on the wafer. On the polished wafer surface, there is topographic fluctuation,

caused by differences in thickness and torsion of the crystal structure. This fluctuation is normally less than 10 micron on the whole wafer surface (10-20 cm), which is much larger than the polished thickness (1 micron or less). During polishing, especially when the pad is hard, some portions of the wafer may be underpolished, and other portions may be overpolished due to roughness of the wafer.

Accordingly, a need exists for the development of an advanced ceramic with sufficiently low brittleness and high thermal shock resistance that does not contain metal oxides. A need also exists for the development of a low cost manufacturing method for producing inexpensive advanced ceramics to make their real-world applications more attractive. A need further exists for the development of a polishing pad that combines the qualities of extended useful life and improved uniformity in the practice of the polishing process. It is therefore toward the fulfillment of these needs in the semiconductor industry and other related industries that the present invention is directed.

DESCRIPTION OF PRIOR ART

The following discussion is provided for review of the state of the art, and includes reference to Figures 1-4. Accordingly, Fig. 1 is a schematic depiction of a silicon wafer in accordance with the prior art. The silicon wafer (11) may contain several hundred chip dies (12). The high density areas of transistors (13) are normally on the central portion of the dies, and the low density areas (14) are normally on the edge portion of the dies. For the interconnection of transistors, dielectric and conductive materials are alternately deposited on the wafer. The deposition procedure is followed by etching and polishing procedures. The polishing procedure leads to a planarization effect on the surface, which is necessary for the successful performance of the next processing procedure. Fig. 2 is a schematic depiction of the interconnection layer on the wafer after deposition processing. Referring to Fig. 2, ceramic (metal) pattern (22) already exists on the wafer (20) before a metal (ceramic) layer (21) is deposited on the pattern layer. The top surface is not flat, which is caused by different height on the patterned surface. Fig. 3 is a schematic depiction of structure in Fig. 2 after the performance of chemical-mechanical polishing (CMP). The surface of the ceramic (metal)

pattern (22) and metal (ceramic) deposition layer (31) on the silicon wafer (20) is planarized and ready for the next processing procedure.

Chemical-mechanical polishing is the dominant planarization technique for the preparation of the functional layers on silicon wafers. Fig. 4 is the schematic depiction of basic polishing equipment. The polishing pad (43) is fixed on the platen (41) with rotating structure (42). Silicon wafer (44) is fixed to the holder (45). Pressing, displacing and rotating structure (46) forces the wafer down to the polishing pad. The slurry supplier (47) supplies polishing slurry, which normally comprises a chemical solution and nanophase abrasives. The polishing pad is normally made of porous materials. The open pores work as a drain for slurry flow and polishing by-products.

Polishing pads with high rigidity have been studied by many researchers in the field. U.S. Patent No. 5,197,999 discloses a composite polishing pad which includes a soft matrix and a substance for stiffening distributed in the pad so as to effect such stiffening of pad. The suggested stiffening materials are hard particles and fiber. However, these materials are frequently too hard; if they stick out of the pad surface, scratching occurs. U.S. Patent Nos. 5,212,910 and 5,287,663 both disclose a multi-layered pad. On a hard substrate, the top layer is made of a very thin porous polymer material (e.g. less than 0.1 mm). However, this thin layer has to be replaced often. Toshirin, et al. (1995 International Symposium on Semiconductor Manufacturing, pp. 214-217) suggest a non-porous pad made of high stiffness polymer. The grooves on the surface work as channels for better slurry flow.

K. S. Mazdidasni et al. made a composite of Si_3N_4 and h-BN with 6% CeO_2 under the conditions of 1800°C and 34.5 MPa (J. of Am. Ceram. Soc., Vol. 64, No.7, 1981, pp.415-419) and a composite of AlN and h-BN under the condition of 1800-2000 °C and 11.5 MPa (Am. Ceram. Soc. Bull., Vol. 64, No.8, 1985, pp. 1149-1154). The BN/ Si_3N_4 composite showed improved electrical and thermal shock behavior. Kanai et al. (Japanese J. of Applied Physics, Vol.31, No. 5A, 1992, pp. 1426-1427) made a composite of h-BN and AlN under the conditions of 1800°C and 40 MPa. The toughness ($4.4 \text{ MPa m}^{1/2}$) of the BN/AlN (30/70) composite is greater than that ($4.0 \text{ MPa m}^{1/2}$) of pure AlN. W. S. Coblenz et al. (J. Am. Ceram. Soc., Vol. 71, No. 12, pp. 1080-1085) made a composite of h-BN and Al_2O_3 and/or

SiO₂, using a reaction of B₂O₃ with Al₂O₃ and/or Si₃N₄. The mechanical properties of these composites show a strong anisotropy caused by the anisotropy of the h-BN crystal. The thermal conductivity of the h-BN-AlN composite shows up to 10 fold difference at different directions. The mixtures of B₂O₃ with Al₂O₃ and/or Si₃N₄ powder were compressed at a temperature lower than 1000°C, and then sintered at a temperature over 1600°C. The majority of the h-BN composites described in the above publications contain metal oxides as sintering additives. In one experiment of Coblenz et al. (J. Am. Ceram. Soc., Vol. 71, No. 12, pp. 1080-1085) where Si₃N₄ is reacted with B₂O₃ to form SiO₂ and BN, the resultant composite is characterized as a composite of ceramics and glass. Its continuous glass phase makes it very different in behavior from ceramic composites.

All of the references discussed above fail to appreciate or suggest the special needs and objects relevant to the methods and the associated polishing pad as applied to semiconductor wafer surface finishing.

SUMMARY OF THE INVENTION

In one aspect, the present invention is related to the use of hexagonal boron nitride (h-BN) and composites including h-BN as polishing pad material. Its higher modulus than that of synthetic polymeric material makes a pad more rigid, which in turn, when used in chemical-mechanical polishing in the semiconductor industry, leads to a high planarity on the die surface. The hardness of hexagonal boron nitride is much lower than that of normal ceramics, which keeps scratching from occurring on the die surface.

The present invention also provides polishing pad constructions particularly well suited for the processing of silicon wafer surfaces. The polishing layer comprises one or more polishing blocks, preferably having a polygonal shape, which are made of hexagonal boron nitride or its composite. This new polishing layer has a high rigidity which leads to a high planarity on the die surface. In the case of a multi-block pad, the blocks are mounted with certain gaps between one another on the elastic layer or a rigid thin layer, which in turn is mounted on the elastic layer. The elastic layer may be either an intact or continuous layer disposed over the entire base, or may be separated with similar gaps. Deformation of the elastic layer during

the polishing process allows the separated blocks to adjust their individual positions in order to adapt to the fluctuating configuration of the wafer surface, which produces a high polishing uniformity on the whole wafer surface. The rigid thin layer decreases the possibility and extent of unwanted impact, when the elastic layer deforms, between the wafer edge and adjacent polishing blocks due to the difference in height among the blocks underneath the wafer and the blocks around the wafer. It also keeps the blocks immediately surrounding the wafer edge tilted towards to the wafer edge.

Accordingly, and in a first embodiment of the present invention, a polishing pad is disclosed which comprises:

- 10 (a) a rigid base or substrate; and
- (b) at least one polishing block mounted on said substrate, said block having a height of 1-50 mm and an elastic modulus of at least 1 GPa.

In a further embodiment of the invention, a polishing pad is disclosed which comprises:

- 15 (a) a rigid base or substrate;
- (b) an elastic layer mounted on said substrate, said elastic layer being 0.1-10 mm thick; and
- (c) at least one polishing block fixed on said elastic layer with adhesives, said block having a height of 1-50 mm and an elastic modulus of at least 1 GPa.

In a yet further embodiment of the invention, a polishing pad is further disclosed which

- 20 comprises:
- (a) a rigid base or substrate;
- (b) an elastic layer mounted on said substrate, said elastic layer being 0.1-2 mm thick;
- (c) a thin layer mounted on said elastic layer, said thin layer having a thickness from 0.01 mm to 1.0 mm and an elastic modulus of at least 1 GPa; and
- 25 (d) at least one polishing block fixed on said elastic layer with adhesives, said block having a height of 1-50 mm and an elastic modulus of at least 1 GPa.

More particularly, said thin layer is made of rigid or resilient material polymer or metal.

The present invention also provides a polishing pad comprising compressed granules.

The present invention also provides a polishing pad comprising at least one groove on the free surface of said block.

The present invention further provides a polishing pad comprising a pore-forming material.

- 5 It is further an object of the present invention to provide a apparatus for polishing comprising one or more polishing pads which in turn have at least one opening. The introduction of opening(s) into polishing pad will facilitate polishing slurry flow so that more even polishing rate will be achieved. Such an apparatus for polishing further comprises:

- 10 (a) a rotating platen on which said polishing pad is fixed;
(b) a plurality of wafer holders;
(c) a pressing, displacing, and rotating structure; and
(d) a slurry supplier.

- It is another object of the present invention to provide new processing methods of making a pad containing hexagonal boron nitride or its composite. Low porosity of such a pad makes
15 the composite rigid, and its large pore size provides sufficient draining ability.

In particular, a method of making a pure hexagonal boron nitride pad is disclosed, which comprises:

- (a) pressing a quantity of nano powder of hexagonal boron nitride in a mold;
(b) sintering said hexagonal boron nitride from Step (a) in a nitrogen atmosphere at a
20 temperature between 1600 to 2300°C for a period of time between 1 hour and over 10 hours.

A pore-forming material may be mixed with said hexagonal boron nitride before said pressing Step (a).

Another method of making a hexagonal boron nitride pad is disclosed, which comprises:

- 25 (a) mixing ceramic powder with a solution having a boron-containing compound;
(b) stirring said mixture from Step (a);
(c) heating said mixture from Step (b) to over 200°C;

(d) pressing said mixture from Step (c) in a mold at a temperature between room temperature and 450°C under a pressure between 30 MPa and over 200 MPa;

(e) sintering said mixture from Step (d) in a nitriding furnace wherein ammonia is used as a reaction gas at a temperature between 450°C and 990°C;

5 A method of making hexagonal boron nitride composite for polishing is further disclosed, which comprises:

- (a) mixing hexagonal boron nitride and a polymer;
- (b) granulating the mixture of Step (a); and
- (c) forming the granulate of Step (b), and curing the resulting formed composite.

10 Particularly, a hot water treatment may be performed after granulation which comprises:

- (a) mixing granules from said granulation in hot water;
- (b) stirring said mixture from Step (a); and
- (c) cooling said mixture from Step (b).

15 More particularly, said granulation step comprises:

(a) dissolving one or more polymers and one or more curing additives in an organic solvent;

- (b) mixing of ceramic particles and surfactant in said solution of (a);
- (c) drying of said mixture from Step (b);

20 (d) loading and stirring said mixture from Step (c) in hot water;

- (e) cooling said mixture from Step (d); and
- (f) filtering, flashing, drying said mixture from Step (e).

A hot water treatment may be performed after drying in Step (f) above, which comprises:

- (a) mixing granules from said granulation step in hot water;
- 25 (b) stirring said mixture from Step (a); and
- (c) cooling said mixture from Step (b).

In a further and important aspect of the invention, a coating step to be performed following said granulation step is further disclosed, which comprises:

(a) mixing granules from said granulation with an organic solution of a coating polymer;

(b) loading the mixture from Step (a) into water; and

(c) stirring said mixture from Step (b).

5 A hot water treatment for improving granular structure is also disclosed, which comprises:

(a) mixing granules from granulation in hot water;

(b) stirring said mixture from Step (a);

(c) cooling said mixture from Step (b).

10 Finally, a method of making granules in manufacture of composite materials is also disclosed, which comprises:

(a) dissolving one or more polymers and one or more curing additives in an organic solvent;

(b) mixing of ceramic particles and surfactant in said solution of (a);

(c) drying of said mixture from Step (b);

15 (d) loading and stirring said mixture from Step (c) in hot water;

(e) cooling said mixture from Step (d); and

(f) filtering, flashing, and drying said mixture from Step (e).

A coating step may be further performed following said Step (f) above, comprising:

20 (a) mixing granules from said granulation with an organic solution of a coating polymer;

(b) loading the mixture from Step (a) into water; and

(c) stirring said mixture from Step (b).

Other objects and advantages will become apparent to those skilled in the art from a review the ensuing specification taken in conjunction with the following illustrative drawings.

25 **BRIEF DESCRIPTION OF THE DRAWINGS**

FIGURE 1 is a schematic depiction of a silicon wafer with chip dies.

FIGURE 2 is a cross sectional view of the wafer with pattern and deposit layer before polishing.

FIGURE 3 is a cross sectional view of the structure in Fig. 2 after polishing.

FIGURE 4 is a schematic view of the basic design of the polishing pad and apparatus.

5 FIGURE 5 is a schematic view of a ring-type polishing pad.

FIGURE 6 is a cross sectional view of a two-layer structured polishing pad.

FIGURE 7 is a cross sectional view of a three-layer structured polishing pad.

FIGURE 8 is a cross sectional view of a four-layer structured polishing pad: (A) the pad; (B) the schematic of deformation of the pad under the pressure of wafer.

10 FIGURE 9 schematically illustrates processing procedures of a polishing pad made of hard spheres with soft coating: (A) a hard sphere or granule; (B) a hard sphere or granule with a soft coating; (C) a cross section view of a polishing pad containing such spheres or granules.

DETAILED DESCRIPTION OF THE INVENTION

The polishing pad widely used in the semiconductor industry is in the form of a single plate as shown in Fig. 4. The present invention includes three types of new polishing pads.

Hexagonal boron nitride (h-BN), is used as a pad material which enhances the properties of the composites of pad materials.

The first type is shown in Fig. 6. This type of polishing pad comprises one or more polishing blocks (61) having an elastic modulus of at least 1 GPa. The block is preferably made of
20 hexagonal boron nitride or its composite. The block is polygonally shaped, and is mounted as with adhesives on a base or substrate (62) made of rigid material such as stainless steel. The hexagon shape is preferred for the block. The lateral size of the polygon is from 5 mm to 100

mm, which should be larger than that of a die on a wafer. The height of the block is from 1 mm to 50 mm. It is preferred that more than one block is used. The gap between adjacent blocks is preferably from 0.1 mm to 10 mm. The gap between the blocks can work as a trench which supply and drain the polishing slurry and polishing by-products. On the top surface of a block, one or more grooves may be made to help the slurry flow.

The second type of new polishing pad is shown in Fig. 7. It is the same as the first type except that an elastic layer (73) is inserted between the blocks (61) and the rigid substrate (62). The thickness of the elastic layer is from 0.1 mm to 10 mm. The elastic layer can be a whole plate of elastic materials such as polymer and rubber covering the entire base. It may also be separated underneath each polishing block. The larger lateral size of a block than that of a die ensures a high degree of planarization effect on the surface of each die. During the polishing process, the elastic layer is compressed under a downward force. Fluctuation in wafer configuration makes the magnitude and direction of the pressure variable on different blocks. Deformation of the elastic layer underneath the block will allow each block to independently follow the instant configuration of a wafer surface. This provides a high polishing uniformity on the whole wafer surface, regardless of any topographic fluctuation prior to the polishing process.

The four-layer polishing pad is shown in Fig. 8A. It has the same structure as the three-layer pad except that a thin rigid layer made of material such as polymer or metal (84) is inserted between the polishing blocks (61) and the elastic layer (73). This thin layer has high rigidity or resilience. Its thickness is from 0.01 mm to 1.0 mm. Its modulus is at least 1 GPa. When the wafer is loaded with a downward force (86) as shown in Fig. 8B, the polishing block(s) directly underneath the wafer (85) will be depressed lower than other adjacent polishing blocks immediately surrounding the wafer edge. This difference in polishing block height may lead to impact between the wafer edge and the blocks immediately surrounding the wafer during the rotation of the wafer and pad. By introducing the rigid thin layer (84) layer between the polishing block(s) (61) and the elastic layer (73), those adjacent block(s) around the wafer edge will also be pulled or forced down during wafer rotation as shown in Fig. 8B, which decreases the height difference among the polishing blocks directly underneath the wafer (85) and the surrounding blocks. On the other hand, these immediately adjacent blocks

will tilt towards the wafer edge as shown in Fig. 8B. This pulling effect of the rigid thin layer decreases the probability and extent of the impact between wafer edge and its surrounding polishing blocks.

A polishing pad (51) can bring better slurry flow and more even polishing rate than a conventional disc pad currently used in the field when it has one or more openings in it, such as in the simple case of a ring-shaped pad exemplified in Fig. 5. The lateral displacement of the wafer (44) holder (45), controlled by rotating and displacing apparatus (46), makes the fringe portion of the wafer move outside the inner or outer edge of the pad, which decreases the polishing rate on the fringe portion of the wafer. After a careful adjustment of the distance and speed of the lateral displacement of the wafer holder, the uneven polishing rate on the fringe portion and the central portion of a wafer can be significantly decreased or nearly eliminated.

The present invention further relates to the use of pure hexagonal boron nitride or a composite of hexagonal boron nitride, e.g. with a polymer material and/or an inorganic material, to make the block or blocks of a polishing pad which, as a result, has high rigidity and yet low enough hardness so that no scratching will occur on the surface of a wafer. More particularly, the composite may be prepared from and may comprise hexagonal boron nitride, a polymer, and other inorganic materials, including ceramics. Further and by way of non-limiting example, such ceramics may include compounds of molybdenum and tungsten, and particularly, molybdenum disulfide (MoS_2), molybdenum diselenide (MoSe_2), molybdenum ditelluride (MoTe_2), tungsten disulfide (WS_2), and tungsten ditelluride (WTe_2). These latter materials exhibit a hardness that is reduced from that of h-BN and can serve in this capacity, as solid lubricants in the final composite article. The amount of these materials to be included may vary within the parameters for the inorganic material component as recited later on herein.

Referring further to the method of making the polishing pad, the common sintering method for the preparation of hexagonal boron nitride parts uses boron oxide and metal oxides as sintering additives. Metal oxides have high hardness, and will lead to scratches on the wafer surface. In the present invention, pure hexagonal boron nitride is used instead. A pure

hexagonal boron nitride pad can be produced, e.g. by a method such as that described as follows below.

The first method is high temperature sintering of nano powder of hexagonal boron nitride without metal oxide additives. Hexagonal boron nitride with a nano size (less than 100 nanometer) has larger surface energy than normal ceramics, which leads to a much better sinterability. A new sintering process of producing pure hexagonal boron nitride part without the metal oxides as additives is presented herein. Nano powder of hexagonal boron nitride is pressed in a mold. The green body is then sintered in a nitrogen atmosphere at a temperature between 1600 to 2300°C for a period of time between 1 hour and over 10 hours. In a particular embodiment, a temperature of 1900-2000°C and sintering time of 3 to 5 hours are preferred. At high temperature, hexagonal boron nitride powder connects together and grows up via solid diffusion. The density of the sintered product depends on the density of the green body. A lubricant liquid mixed with the raw powder before pressing can increase primary density. Water and organic liquids such as acetone may be used as the lubricants. To increase strength of the product, carbon is used to reduce the boron oxide on the surface of the hexagonal boron nitride powder. The raw powder is mixed with a solution of a surfactant and an organic compound such as glucose.

After drying by a process such as spray drying, the powder surface is coated with a thin layer of an organic compound. The powder is then heated in an inert atmosphere at a temperature of 200-600°C. After the pyrolytic reaction of the organic compound, very fine carbon particles are left on the surface of the hexagonal boron nitride powder. During the sintering process, these carbon particles can reduce the boron oxide naturally produced on the surface of hexagonal boron nitride. The amount of carbon may range from 0.1% to 5%, with 1-2% of carbon content being preferred. The porosity of the product is from 35% to 55%, depending on the density before sintering. The rupture strength is from 10 to above 20 MPa.

Another method to produce a boron nitride pad is the bonding of boron oxide by a nitriding reaction. Ceramic powder is mixed with a solution of boric acid or other boron containing compounds. Hot water is preferred as the solvent. Other organic solvents such as acetone, and the like are also available. The mixing process is preferably performed with a stirring of

the mixture. The mixture is next dried to remove the solvent. Then the dried mixture is further heated up to over 200°C to make boric acid or other boron containing compounds decomposed into boric oxide. The mixture of boron oxide with ceramic powders is pressed in a mold. Next, the green body is loaded into a nitriding furnace. In the furnace, ammonia is used as the reaction gas. The nitriding temperature may range from about 450°C to about 990°C, with a temperature ranging from about 600°C to about 700°C being preferred. A lower temperature will decrease the reaction rate, while a higher temperature will increase the loss of boron oxide via evaporation. In the furnace, boron acid reacts with ammonia to produce hexagonal boron nitride and water. A set of fans may be used to improve gas flow.

The reaction product, hexagonal boron nitride, bonds the ceramics together and forms a porous composite. The porosity is from 50% to 25%, depending on forming pressure and temperature. The forming temperature is from room temperature to over 450°C (the melting point of boron oxide), and the forming pressure is from 30 MPa to over 200 MPa. The mixture of boric acid with ceramic powder can be directly formed in a mold without de-water reaction of boric acid, but in doing so the final porosity will be over 50%. A pure hexagonal boron nitride part with high purity and porous structure can be produced by this process when hexagonal boron nitride is used as the original ceramic material.

Abrasives with nano size may also be mixed with boric acid and/or hexagonal boron nitride in a liquid solution (water or organic liquid such as acetone) containing a surfactant such as silane coupling agent, under a strong stirring. This allows the abrasives to be separately distributed in the formed slurry. The added amount of the surfactant is from 0.1% to 10% of the weight of the inorganic substances, depending the surface area of the inorganic compounds. After drying by a process such as spray drying, an evenly distributed mixture is ready for sintering or nitriding reaction.

Before sintering or nitriding, pore-forming materials such as latex balls with low volatilization point or decomposition temperature can be added into the green body if increased amount of large pores is desired.

Further with regard to the method of the present invention, a three-step method of making composites including hexagonal boron nitride, a polymer material and optionally, other

inorganic materials as discussed above, is disclosed herein, which may be used as polishing pad materials or in other cases where abrasion of a work piece is desired.

The first step is mixing of the polymer and hexagonal boron nitride and/or other inorganic materials. Regular polymers or their precursors are too sticky to make an evenly distributed mixture with ceramic particles. To decrease viscosity, a solvent such as water or an organic solvent is used to dilute the polymer.

In the second step the mixture is turned into granules. Well-known procedures such as spray drying, spray cooling, extraction of solvent from emulsion and the like are available. Spray drying is inexpensive and is the most popular method. A disadvantage of spray drying is that the dried particles always have defects such as hollow cavities.

A new procedure of making a granular mixture is disclosed as follows. The raw materials are water insoluble thermosetting polymer or its mixture with other polymer as well as inorganic enhancement such as ceramic powders. The polymer should have a high curing temperature, which is preferred to be over 100°C, or more preferably over 150°C. Its melting point should be higher than room temperature, but not higher than 100°C. The curing additive should also be water insoluble. An organic solvent, such as acetone, is used to dissolve the polymer and the curing additive, then the solution is mixed with ceramic particles (abrasives and/or h-BN) and a surfactant (such as a silane coupling agent). Water is added in the prepared mixture in a controlled speed and steps with a stirring. The solvent, such as acetone, will be extracted gradually by water, and the solid granules of the mixture will gradually form. After removal of the organic solvent, the mixture is loaded in a container of hot water. The temperature of the hot water is higher than the melting point of the polymer. Stirring is used to make the emulsion of liquid polymer mixture, which forms many droplets of the mixture in the hot water. Stirring condition determines the size of the droplets. The droplets will form spheres with little or no voids inside. The system is then cooled, of which adding cold water is a convenient method. When the temperature drops below the melting point of the polymer, the droplets transform into the solid granules. After filtering, flashing and drying, the granules are ready to be sieved into different groups by size. The granules with a

desired size are taken to the next step. The granules with smaller or larger sizes may be recycled for further processing.

The third step is forming and curing. The granules are loaded in a mold, and pressure is applied. Deformation of the granules under pressure brings them into close contact with each other. Then the green body is cured in a furnace. The volume fraction of the inorganic materials may range from about 5% to about 90%. The porosity may range from about 5% to about 60%, depending on the forming conditions and the volume fraction, size and shape of the inorganic materials.

The following procedures are used to improve the structure and function of granules.

(1) Hot water treatment

The polymer in granules should be water-insoluble, and has a melting point lower than 100°C. Primary granules with defects are loaded in the water and stirred. When the temperature of the water is over the melting point of the polymer, the polymer melts, shrinks, and consequently liquid granules are transformed into perfect spheres without or with much less defects such as cracks, voids, and the like. This is followed by cooling which solidifies the granules again.

(2) Granular coating

Preferably the granules are further coated with a coating polymer. The coating polymer should be water-insoluble and can be used as an adhesive at the curing temperature of the granules. The same polymer used in the granules is preferred. No or very little hexagonal boron nitride is added in the coating polymer. The granules are mixed with an organic solution of a coating enhancement, such as h-BN or polymer before or after curing. The organic solvent in this solution should be water soluble. The mixture is loaded in the water and stirred, and an emulsion forms. The organic solvent is then gradually extracted into water, and at the same time the granules are coated with a layer of the polymer. The coated granules are then pressed in a mold and cured.

Consequently, the surface of the product such as a polishing pad will have two areas as depicted in Fig. 9. The hard area consists of the core portion of the granules (91), while the soft area consists of the polymer coating (92) which has lower wear resistance. During polishing, a selective wear occurs on the pad surface (94) because of the difference in wear resistance. The wear rate of the coating portion will be higher, especially under slurry erosion. The lowered surface of the eroded coating portion forms an additional groove (95) network throughout the whole surface, which improves slurry transportation. This groove network is continuously and automatically refreshed (formed and re-formed), and forms a 3-dimensional network with the open pores (93) inside the blocks. The selective wear of the pad surface can be adjusted by changing the composition of the coating polymer and/or the adding a varying amount of hexagonal boron nitride in an adequate ratio less than in the core. Such adjustment can make grooves for improving slurry flow and keep an adequate bonding for granules at the same time. The thickness of the coating layer is preferably from 10 microns to 2 mm.

- 15 The block(s) of polishing pad are made by the above procedures. Cross-linking resins such as polyurethane resin, epoxy and the like can be used to make granules with hexagonal boron nitride powders. The volume fraction of hexagonal boron nitride in core granules shown in Fig. 9A is from 30% to 60%; 40-50% is preferred. The particle size of h-BN is from smaller than 100 nm to above several micron. The granule size is from 10 microns to 5 mm. The preferred granule size is from 0.1 mm to 0.5 mm in diameter. The high rigidity of the present new pad materials comes from the elastic modulus of hexagonal boron nitride higher than that of polymers. Meanwhile, the present new pad materials also have a lower porosity than that of a foam polymer with open pores. In the case of a polishing pad having foam materials which is current in wide use, the porosity is kept as high as 70-80% so that a high fraction of open pores are maintained for slurry flow. This, however, makes the foam structure weak and much less rigid. On the other hand, the open pore structure, shown as 93 in Fig. 9, of the new pad composite disclosed above comes from the gaps between the adjacent granules. The larger the granules, the larger the size of the open pores. The porosity of the products can be from 20% to 40%, which is much less than that in open pore foam materials (70-80%) and makes the composite hard and rigid.
- 20
25
30

The nano abrasive particles, such as oxides including silica and CeO, carbides, nitrides and the like with a surfactant may be added in the green body in each of the above processing methods. Preferably hexagonal boron nitride and an abrasive in nano size, such as silica powder, are mixed with a surfactant such as silane coupling agent and a water insoluble polymer in an organic solution such as acetone, under a strong stirring. The amount of the surfactant added is preferably from 0.1% to 10% of the weight of the inorganic compounds. A polishing pad with fixed or semi-fixed abrasives will change the polishing process parameters. The slurry with abrasives may be replaced by liquid solution or even pure water.

The present invention will now be further described and illustrated by the following examples, wherein unless expressly stated, all process parameters, units of measurement and the like, are intended to have their art recognized meanings.

EXAMPLE 1

The mixture of 40 v% B₂O₃ and SiC, is nitrided at a temperature of 630°C for 10 hours. On the surface of the used SiC particles, there is a layer of SiO₂ which is about 9% of total SiC particles. After the nitriding reaction, about a half of B₂O₃ is transferred into h-BN and another half is transferred into a glass of B₂O₃ and SiO₂.

EXAMPLE 2

High purity h-BN products with a thickness of 5-6 mm are nitrided in a 10 hour reaction at 630 °C. The primary mixture has a 30 v% of boron oxide. The product formed at room temperature and under a pressure of 180 MPa has a porosity of 40-45% and have less than 1% of the residual boron oxide. The product formed at a temperature between 200°C and 460°C and under a pressure of 80 MPa has a porosity from 40% to even lower than 30% and have 1.0-1.5% of residual boron oxide. The rupture strength of both products is 7-10 MPa. If the residual boron oxide is not counted as impurity, such h-BN products may be considered pure. High purity h-BN products 2-3 mm thick made in accordance with this process has less than 0.5% residual boron oxide.

EXAMPLE 3

Hexagonal boron nitride with a nano size (less than 100 nanometer) has larger surface energy than normal ceramics, which leads to a much better sinterability. Pure hexagonal boron nitride part without metal oxides as additives is produced as follows:

- 5 Nano powder of hexagonal boron nitride with an average size of 60 nm is pressed in a mold. The green body is then sintered in a nitrogen atmosphere at a temperature of 1900-2000°C for a period of time of 3 to 5 hours (1800-2300°C and 1 hour to over 10 hours are available). The resultant high purity h-BN products have a rupture strength of 7-10 MPa.

EXAMPLE 4

- 10 The raw h-BN powder with an average size of 60 nm is mixed with a silicane compound water solution (0.1% to 10% of the weight of the inorganic substances) and glucose. After spray-drying, the powder then is heated in an inert atmosphere at a temperature of 200-600°C before it is sintered in a nitrogen atmosphere at a temperature of 1900-2000°C for 3 to 5 hours. The amount of pyrolyzed carbon is from 0.1% to 5%, and 1-2% of carbon content is preferred. The porosity of the product is from 35% to 55%. The rupture strength is from 10
15 to over 20 MPa. The residual boron oxide impurity is less than 0.5%.

EXAMPLE 5

- The electrically conductive, refractory diborides, in particular TiB_2 , are used as an electrode material in high temperature applications. These range from resistive sources for the
20 vaporization of metals to anode and cathode materials in the production of aluminum. For densification of TiB_2 , Nickel (Ni) and boron oxide (B_2O_3) are used to form a low melting point secondary boride phase. The molten metals such as aluminum will attack these low melting point phase and decrease the lifetime of the composite. The following is an improved way to prepare ceramic composites for manufacturing electrodes with an elongated lifetime.

Boric acid solution having B_2O_3 equivalent to 5 v% (up to 50 v% is available) is mixed with TiB_2 and AlN ($TiB_2:AlN=5:1$). The mixture is then dried and heated to above $150^\circ C$ together with spray drying to decompose boric acid. The green body is further formed at $200^\circ C$ under a pressure of 80 MPa. A high temperature treatment at $1700-2100^\circ C$ is performed. Then it is
5 nitrided at $630^\circ C$ for 1-5 hours. The product has 0.5-1.0% of residual boron oxide. The high temperature treatment can also be performed after the nitriding reaction to increase the strength of the composite product.

Pure h-BN is more advantageous than the composite of h-BN with metal oxides (usually as sintering additives) in various fields. Since h-BN has a higher modulus than that of synthetic
10 polymeric material currently in wide use, it makes a pad more rigid, which in turn leads to a high planarity on the die surface. Clearly h-BN and its composites represent a better choice of polishing pad material than pure synthetic polymeric material.

Another practical application of high purity hexagonal boron nitride ceramic and its composites is their use in manufacturing crucibles. An apparent technical advantage of h-BN
15 and its composites over other advanced ceramics is its sufficiently low brittleness. h-BN and its composites that don't contain metal oxides are further advantageous, compared with other metal oxide containing ceramics, since they will not cause metal contamination when crucibles are used in experiments involving any sample with ultra high purity.

A pad of the present invention can be used for any other polishing apparatus. It is particularly
20 useful where a high planarity on the polished surface is desirable, but scratching is not. The process of hot water treatment of granules and the method of making granules directly from hot water treatment are also very useful in the manufacture of composite materials which may include, besides boron nitride composite, composites of polymers such as thermosetting resins with or without other inorganic materials such as ceramic powders and short fibers.

25 This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present disclosure is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being

indicated by the appended Claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

I CLAIM:

1. A polishing pad, which comprises:
 - (a) a rigid base or substrate; and
 - (b) at least one polishing block mounted on said substrate, said block having a height
5 of 1-50 mm and an elastic modulus of at least 1 GPa.
2. A polishing pad, which comprises:
 - (a) a rigid base or substrate;
 - (b) an elastic layer mounted on said substrate, said elastic layer being 0.1-10 mm
thick; and
 - 10 (c) at least one polishing block fixed on said elastic layer with adhesives, said block
having a height of 1-50 mm and an elastic modulus of at least 1 GPa.
3. A polishing pad, which comprises:
 - (a) a rigid base or substrate;
 - (b) an elastic layer mounted on said substrate, said elastic layer being 0.1-2 mm thick;
 - 15 (c) a thin layer mounted on said elastic layer, said thin layer having a thickness from
0.01 mm to 1.0 mm and an elastic modulus of at least 1 GPa; and
 - (d) at least one polishing block fixed on said elastic layer with adhesives, said block
having a height of 1-50 mm and an elastic modulus of at least 1 GPa.
4. A polishing pad as in Claim 3, wherein said thin layer is prepared from an organic
20 polymeric material.
5. A polishing pad as in Claim 3, wherein said thin layer is prepared from a metal.
6. A polishing pad as in Claims 1, 2 or 3, further comprising a surfactant and at least one
abrasive.
7. A polishing pad as in Claim 6, wherein said surfactant is a silane coupling agent.

8. A polishing pad as in Claim 6, wherein said abrasive is selected from the group consisting of oxides, carbides, and nitrides.

9. A polishing pad as in Claims 1, 2 or 3, further comprising alternatively arranged hard regions and soft regions on the free surface of said pad.

5 10. A polishing pad as in Claim 9, wherein said hard regions consist of core portions of granules.

11. A polishing pad as in Claim 9, wherein said soft regions consist of coatings of a water-insoluble polymer.

10 12. A polishing pad as in Claim 9, wherein said hard regions consist of the core portion of granules and said soft regions consist of coatings outside said core portions of granules.

13. A polishing pad as in Claims 1, 2 or 3, further comprising a material selected from the group consisting of boron nitride and boron nitride composite.

14. A polishing pad as in Claims 1, 2 or 3, wherein said block is a polygonally shaped and is prepared from a material selected from the group consisting of boron nitride and boron
15 nitride composite.

15. A polishing pad made of a material selected from the group consisting of boron nitride and boron nitride composite.

16. A polishing pad as in Claim 15, further comprising at least one polygonally shaped block made of a material selected from the group consisting of boron nitride and boron nitride
20 composite.

17. A polishing pad as in Claim 15 wherein said boron nitride composite comprises at least one polymer.

18. A polishing pad as in Claim 17, wherein said polymer is selected from the group consisting of thermosetting resins, thermoplastic resins, and elastomers.

19. A polishing pad as in Claim 17 wherein said polymer is selected from the group consisting of epoxy and polyurethane.

5 20. A polishing pad as in Claims 1, 2, 3 or 15, further comprising at least one groove on the free surface of said block.

21. A polishing pad as in Claims 1, 2, 3 or 15, further comprising a pore-forming material.

10 22. A polishing pad as in Claim 18, wherein said pore-forming material is selected from the group consisting of latex and polyurethane.

23. A polishing pad as in Claims 1, 2 or 3, wherein said block has an elastic modulus of at least 3 GPa.

24. A polishing pad comprising compressed granules.

15 25. A polishing pad as in Claim 24, wherein said granules comprising hard regions and soft regions.

26. A polishing pad as in Claim 25, wherein said hard regions are granular cores and said soft regions comprise polymer coatings.

27. A polishing pad as in Claim 26, wherein said granular cores comprise a polymer.

20 28. A polishing pad as in Claim 27, wherein said granular cores further comprises inorganic enhancement.

29. A polishing pad as in Claim 28, wherein said inorganic enhancement is hexagonal boron nitride.

30. A polishing pad as in Claim 26, wherein said soft regions further comprises inorganic enhancement.

5 31. A polishing pad as in Claim 30, wherein said inorganic enhancement is hexagonal boron nitride.

32. A polishing pad as in Claim 25, wherein said granules comprising alternatively arranged hard regions and soft regions on the free surface of said pad.

10 33. Apparatus for polishing comprising at least one polishing pad as in Claims 1, 2, 3 or 15.

34. Apparatus for polishing comprising at least one polishing pad, said pad having at least one opening through its body.

35. Apparatus for polishing as in Claim 34, which further comprises:

- 15 (a) a rotating platen on which said polishing pad is fixed;
(b) a plurality of wafer holders;
(c) a pressing, displacing, and rotating structure; and
(d) a slurry supplier.

36. A method of making a pure hexagonal boron nitride pad, which comprises:

- 20 (a) pressing nano powder of hexagonal boron nitride in a mold;
(b) sintering said hexagonal boron nitride from Step (a) in a nitrogen atmosphere at a temperature between 1600 to 2300°C for a period of time between 1 hour and over 10 hours.

37. A method as in Claim 36, wherein a lubricant liquid is mixed with said hexagonal boron nitride before said pressing Step (a).

38. A method as in Claim 36, wherein the sintering step of Step (b) is performed for a period of time ranging from about 3 to about 5 hours.

39. A method as in Claim 36, wherein the sintering step of Step (b) is performed at a temperature ranging from about 1900 to about 2000°C.

5 40. A method as in Claim 37, wherein said lubricant liquid is water.

41. A method as in Claim 36, which further comprises depositing a layer of carbon particles on the surface of said nano powder before said pressing Step (a).

42. A method as in Claim 41, wherein a solution of a surfactant and an organic compound is mixed with said nano powder of hexagonal boron nitride before said pressing Step (a).

10 43. A method as in Claim 42, wherein said organic compound is glucose.

44. A method as in Claim 36, wherein a pore-forming material is mixed with said hexagonal boron nitride before said pressing Step (a).

45. A method of making a hexagonal boron nitride pad, which comprises:
15 (a) mixing ceramic powder with a solution having boron containing compound;
(b) stirring said mixture from Step (a);
(c) heating said mixture from Step (b) to over 200°C;
(d) pressing said mixture from Step (c) in a mold at a temperature between room temperature and 450°C under a pressure between 30 MPa and over 200 Mpa; and
(e) sintering said mixture from Step (d) in a nitriding furnace wherein ammonia is
20 used as a reaction gas at a temperature between 450°C and 990°C.

46. A method as in Claim 45, wherein said ceramic powder is hexagonal boron nitride.

47. A method as in Claim 45, wherein a drying step is performed after stirring and before heating.

48. A method as in Claim 47, wherein said ceramic powder is hexagonal boron nitride.

49. A method of making hexagonal boron nitride composite article for polishing, which comprises:

- (a) mixing hexagonal boron nitride and a polymer;
- 5 (b) granulating the mixture of Step (a); and
- (c) forming the granulate of Step (b) into said composite article and curing said article.

50. A method as in Claim 49, wherein a hot-water treatment is performed after granulation, said hot water treatment comprising:

- 10 (a) mixing granules from said granulation in hot water;
- (b) stirring said mixture from Step (a); and
- (c) cooling said mixture from Step (b).

51. A method as in Claim 49, wherein said granulation step comprises:

- (a) dissolving one or more polymers and one or more curing additives in an organic solvent;
- 15 (b) mixing of ceramic particles and surfactant in said solution of (a);
- (c) drying of said mixture from Step (b);
- (d) loading and stirring said mixture from Step (c) in hot water;
- (e) cooling said mixture from Step (d); and
- (f) filtering, flashing, drying said mixture from Step (e).

20 52. A method as in Claim 51, wherein a hot water treatment is performed after drying in Step (f), said hot water treatment comprising:

- (a) mixing granules from said granulation step in hot water;
- (b) stirring said mixture from Step (a); and
- (c) cooling said mixture from Step (b).

25 53. A method as in Claim 49, wherein a coating step is performed following said granulation step, said coating comprising:

- (a) curing granules from said granulation;

- (b) mixing said granules with an organic solution of a coating enhancement;
- (c) loading the mixture from Step (a) into water; and
- (d) stirring said mixture from Step (b).

54. A method as in Claim 53, wherein said coating polymer is the same polymer used in
5 said mixing of hexagonal boron nitride and a polymer.

55. A method as in Claim 53, wherein said coating polymer is an adhesive at the curing
temperature.

56. A method as in Claims 50 or 52, wherein a coating step is performed following
granulation, said coating comprising:

- 10 (a) mixing granules from said granulation with an organic solution of a coating
polymer;
- (b) loading the mixture from Step (a) into water; and
 - (c) stirring said mixture from Step (b).

57. A method as in Claim 56, wherein said coating polymer is the same polymer used in
15 said mixing of hexagonal boron nitride and a polymer.

58. A method as in Claim 56, wherein said coating polymer is an adhesive at the curing
temperature.

59. A hot water treatment for improving granular structure, comprising:

- 20 (a) mixing granules from granulation in hot water;
- (b) stirring said mixture from Step (a);
 - (c) cooling said mixture from Step (b).

60. A method of making granules in manufacture of composite materials, which
comprises:

- 25 (a) dissolving one or more polymers and one or more curing additives in an organic
solvent;

- (b) mixing of ceramic particles and surfactant in said solution of (a);
- (c) drying of said mixture from Step (b);
- (d) loading and stirring said mixture from Step (c) in hot water;
- (e) cooling said mixture from Step (d); and
- 5 (f) filtering, flashing, and drying said mixture from Step (e);

61. A method of Claim 60, wherein a coating step is further performed following said Step (f), said coating comprising:

(a) mixing granules from said granulation with an organic solution of a coating polymer;

10 (b) loading the mixture from Step (a) into water; and

(c) stirring said mixture from Step (b).

FIG. 1

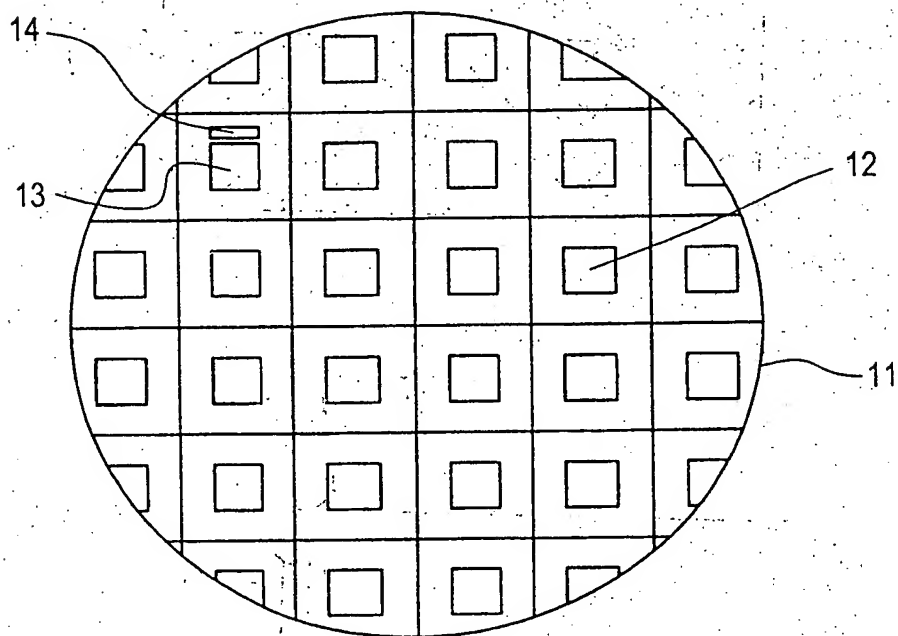
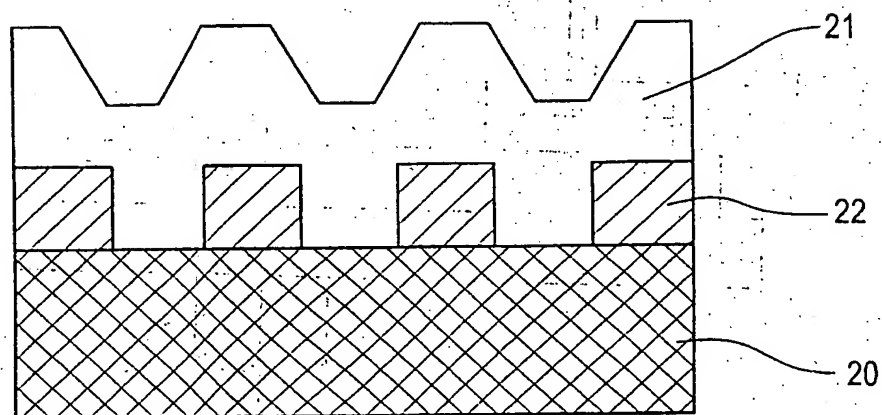


FIG. 2



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FIG. 3

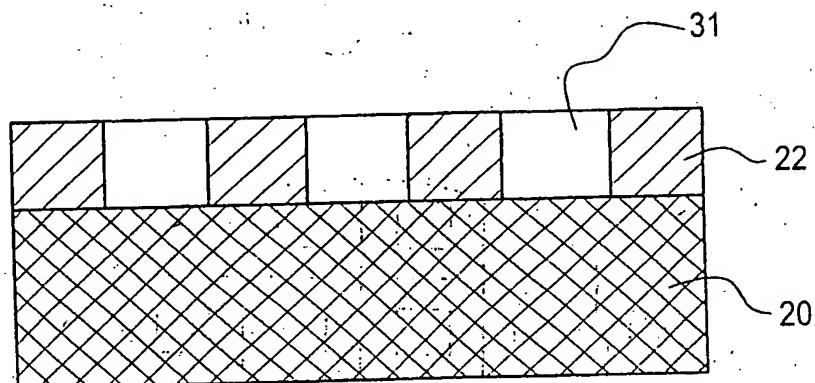


FIG. 4

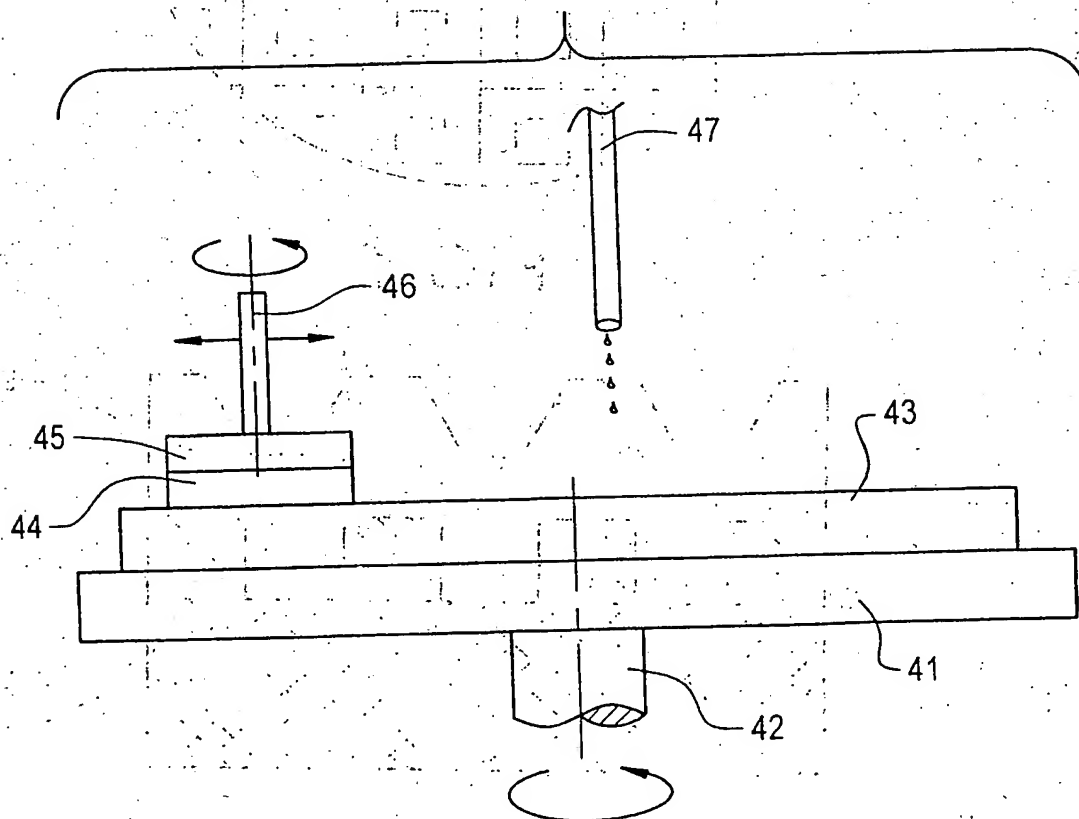


FIG. 5

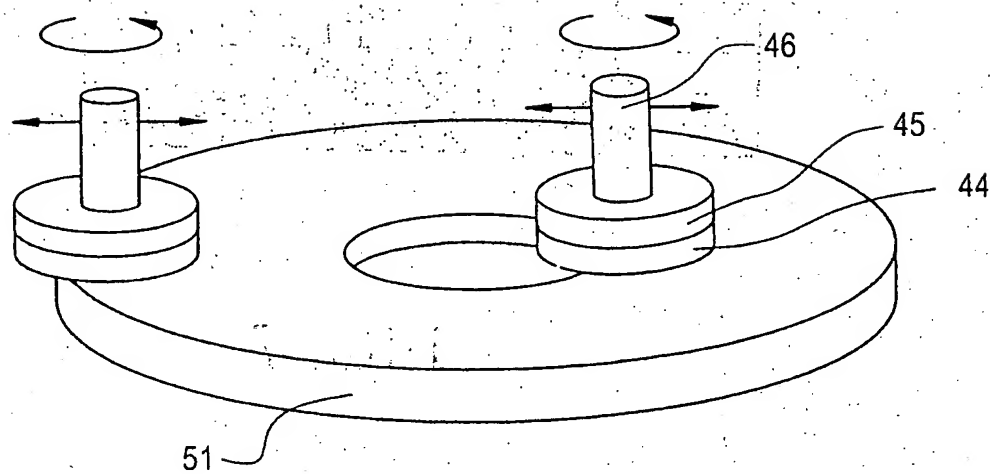


FIG. 6

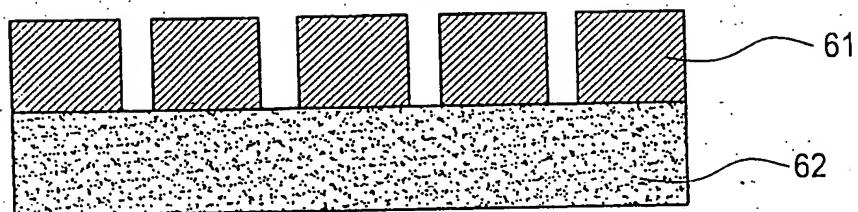


FIG. 7

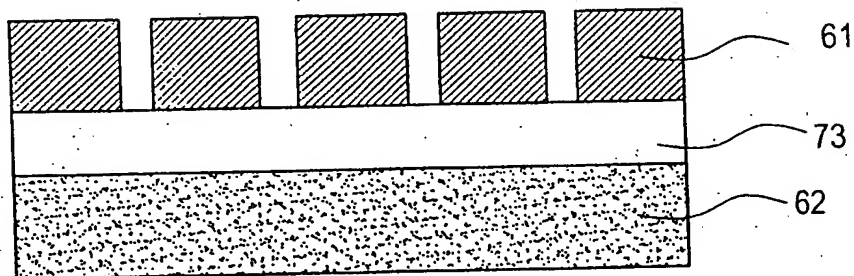


FIG. 8A

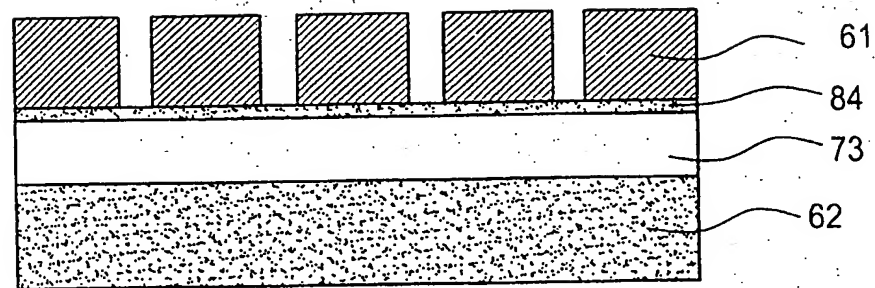


FIG. 8B

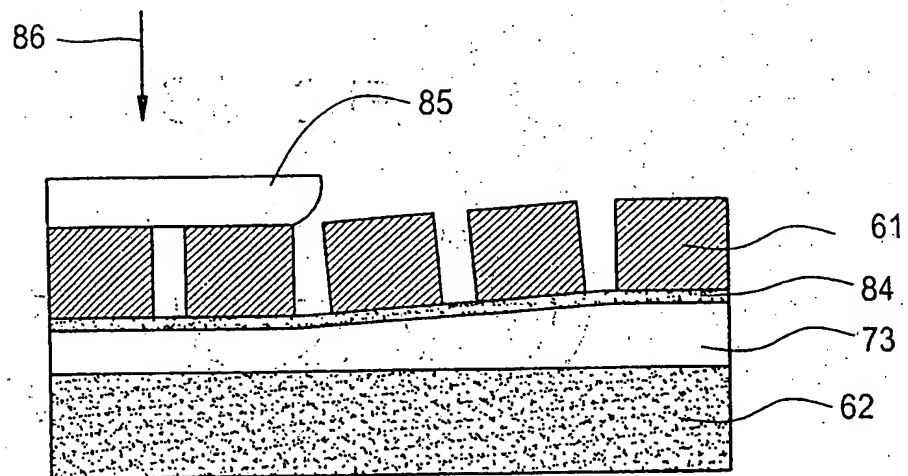


FIG. 9A

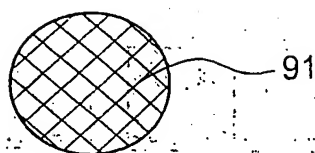


FIG. 9B

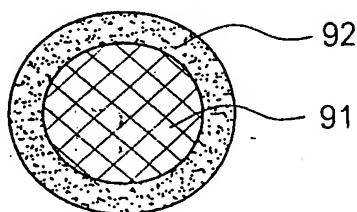
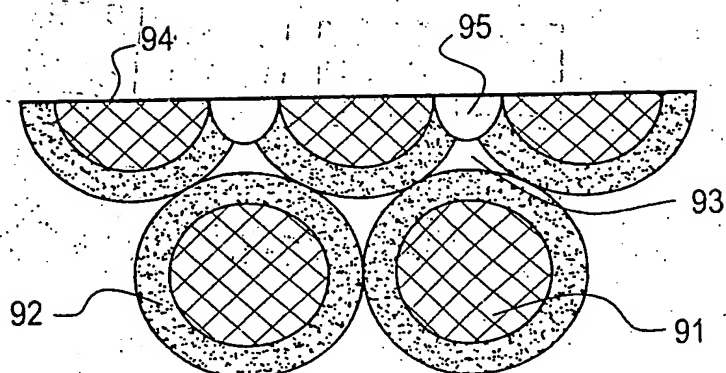


FIG. 9C



INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 98/17720

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B24B37/04 B24D3/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B24B B24D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 095, no. 009, 31 October 1995 & JP 07 164308 A (SHIN ETSU HANDOTAI CO LTD), 27 June 1995 see abstract	1-3
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 153 (M-813), 13 April 1989 & JP 63 312052 A (KASUGAI SEISAKUSHO KK), 20 December 1988 see abstract	15, 16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Z" document member of the same patent family

Date of the actual completion of the international search

27 November 1998

Date of mailing of the international search report

17/12/1998

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/17720

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section PQ, Week 8727 Derwent Publications Ltd., London, GB; Class P61, AN 87-190981 XP002086078 & SU 1 271 725 A (TOOLS RES INST) , 23 November 1986 see abstract</p>	15
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